

Analysis of the elimination process of polymerisation inhibitors from styrene by means of adsorption

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Abstract: This work is focused on the analysis, modelling and scale-up of a process of styrene purification. The first step in synthetic rubber production is to eliminate 4-*tert*-butylcatechol (TBC) which is added to styrene to prevent homopolymerisation during transport and storage. This process is carried out on an industrial scale by means of adsorption onto activated alumina. Equilibrium experiments at 10 °C correlated to the Langmuir–Freundlich equation:

$$q = \frac{1.73 \times 10^{-3} C^{0.50}}{1 + 8.36 \times 10^{-3} C^{0.50}}$$

with a weighted standard deviation of 3.38%. Fixed bed column experiments were carried out on a laboratory scale to obtain breakthrough curves. A mathematical model that considers film and pore mass transfer resistances described satisfactorily the experimental results with a value of $D_p = 3.96 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$ which was obtained from correlation of experimental data to simulated curves. Finally, a pilot plant was built and operated in order to verify the validity of the mathematical model and parameters obtained previously.

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Keywords: styrene; TBC; adsorption; alumina; modelling; scale-up

NOTATION

a_p	External surface area/volume ($\text{m}^2 \text{ m}^{-3}$)	Re	Reynolds number ($\rho_1 u_s d_p \mu^{-1}$)
C_{exp}	Experimental concentration (mg kg^{-1})	Sc	Schmidt number ($\tilde{\mu} D_m \rho^{-1}$)
C_i	Adsorbate concentration (mg kg^{-1})	Sh	Sherwood number ($k_f d_p D_m^{-1}$)
$C_{i,\text{pore}}$	Concentration in pore (mg kg^{-1})	t	Time (s)
$C_{o,i}$	Adsorbate initial concentration (mg kg^{-1})	u_i	Interstitial fluid velocity (m s^{-1})
C_{sim}	Simulated concentration (mg kg^{-1})	u_s	Superficial fluid velocity (m s^{-1})
C^*	Adsorbate equilibrium concentration (mg kg^{-1})	V	Styrene volume (dm^3)
d_p	Particle diameter (m)	V_o	Initial styrene volume (dm^3)
D_m	Molecular diffusivity ($\text{m}^2 \text{ s}^{-1}$)	z	Axial distance in column (m)
D_p	Pore diffusivity ($\text{m}^2 \text{ s}^{-1}$)	ε_e	External void fraction
E	Axial dispersion coefficient ($\text{m}^2 \text{ s}^{-1}$)	ε_p	Particle void fraction
F	Flow rate ($\text{m}^3 \text{ s}^{-1}$)	μ	Viscosity ($\text{kg m}^{-1} \text{ s}^{-1}$)
K_{di}	Fraction of interparticle volume species can penetrate	ρ_l	Liquid density (kg m^{-3})
k_f	Film diffusion coefficient (m s^{-1})	ρ_p	Particle density (kg m^{-3})
k_m	Lumped parameter mass transfer coefficient (m s^{-1})	ρ_s	Structural solid density (kg m^{-3})
m	Weight of alumina (g)		
n	Experimental data number		
q_i	Amount of solute adsorbed onto the solid/amount of solid (kg kg^{-1})		
R_p	Particle radius (m)		

1 INTRODUCTION

Styrene is produced on a large scale (€66 billion pa) mainly for production of styrene–butadiene rubber.¹ The Spanish company Dynasol Elastómeros, which produces 110 000 tons per year of rubber based on

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styrene, has developed an industrial process based on an anionic solution polymerisation reaction using *n*-butyl lithium as initiator; this compound is highly susceptible to contamination by polar compounds such as 4-*tert*-butylcatechol (TBC), which is used as an homopolymerisation inhibitor, leading to an excessive consumption of initiator and delay in the time of reaction. Therefore, the first step in the production process of synthetic rubber is purification of the raw materials, styrene and butadiene.

Styrene polymerisation is usually inhibited with 10–15 mg kg⁻¹ TBC, although concentrations between 10 and 55 mg kg⁻¹ can be acceptable. The rate of TBC depletion varies with storage conditions, particularly with oxygen concentration (in order to have a safety margin 15–20 mg kg⁻¹ of oxygen is preferred), temperature, moisture, rust, and other impurities in the storage vessel.^{2,3}

The effect of inhibitors on the polymerisation of styrene has been studied previously.^{4–7} It has been shown that the existence of small amounts of inhibitors in the feed stream may lead to unstable operation; in particular, oscillatory behaviour and multiple steady-state conditions. Studies have been undertaken on how monomer conversion and relative molecular mass distribution change when different inhibitors are added to an AIBN (2,2-azobis-2-methyl-propionitrile)-initiated styrene solution polymerisation reactor; in particular, monomer conversion and average relative molecular mass decrease continuously as the inhibitor feed concentration increases.⁷ Classic inhibitors based on quinone or phenol structures also lead to lower relative molecular masses than in the uninhibited process.⁶ Experimental studies reveal that inhibitors can have an appreciable effect on polymer growth.⁵

Some authors have compared the elimination of polymerisation inhibitors such as methylhydroquinone (MHQ), *p*-benzoquinone (BQ) and TBC in adsorptive materials such as activated carbon or removal by means of ion exchange resins, reaching the conclusion that the specific surface area is a factor that is likely to affect adsorption to a less significant extent than the polarity of the sorbent.⁸

Adsorption onto alumina is a recognised method to eliminate polymerisation inhibitors from styrene monomer. There are different techniques of preparing alumina in order to improve the efficiency of the purification process.⁹ Alumina is used to purify ethene, propene, butenes, 1-hexene, 1-octene and styrene by adsorbing oxygenated compounds (water, alcohols and, to a lesser extent, aldehydes, esters and ketones). It is also used to remove TBC from styrene, isoprene and butadiene. When fixed beds have been designed for the dual purpose of drying and TBC removal they could be regenerated several times to restore the dessicant capacity before becoming saturated with TBC while this compound cannot be removed by regeneration at temperatures below its decomposition temperature on the alumina surface.

TBC is a special case of alcohol adsorption, as it has two OH groups and is more strongly adsorbed than water.

Nowadays, many industries purify monomers by adsorption onto alumina but the process is empirically controlled. In the case of styrene, the monomer is kept at 10 ± 0.3 °C, it is passed through a fixed bed of alumina and the water content is measured with a moisture probe on line. When water in the outlet styrene stream reaches a non-desirable level (around 10 mg kg⁻¹) the alumina is replaced by a fresh bed. The level of TBC in the styrene outlet is not measured continuously, assuming that its concentration is always less than the concentration of water.

For the design and optimisation of an adsorption column detailed information is required concerning both the equilibrium and kinetics of the separation process. There are several important reviews on this subject^{10–13} although there are few references in the literature on adsorption of organic compounds on alumina.^{14–17}

The aim of this work is to determine the mathematical model and parameters that could predict the adsorption of TBC initially contained in styrene onto alumina. This would contribute to the control and optimisation of the industrial purification process. The first step will be the determination of the equilibrium isotherm at the operating temperature (10 °C) followed by several dynamic experiments carried out on a laboratory scale in order to estimate the characteristic parameters of the model. Finally, predictions at pilot-plant scale will be compared with experimental data in order to verify the mathematical model, and parameters needed, to simulate the industrial process.

2 THEORETICAL BACKGROUND: MASS TRANSFER MODEL

Mass transfer of a solute in a packed bed can be thought of as occurring in several steps. First, the solute diffuses from the bulk fluid to the surface of the particles. This is often treated as occurring across a film. Next, the solute diffuses in the fluid through the pores. Once on the solid, the solute may diffuse along it or it may eventually be desorbed. Once desorbed, the solute may diffuse through the pores back into the bulk fluid or to another site where it will be adsorbed.

The differential mass balance to the solute in the packed bed considering the following hypothesis: (i) the packing is homogeneous, (ii) there are no radial gradients, (iii) there are no chemical reactions and (iv) there are no phase changes other than adsorption, leads to:

$$\varepsilon_e \frac{\partial C_i}{\partial t} + K_{di}(1 - \varepsilon_e)\varepsilon_p \frac{\partial \bar{C}_{i,pore}}{\partial t} + \rho_s(1 - \varepsilon_e)(1 - \varepsilon_p) \frac{\partial \bar{q}_i}{\partial t} + \varepsilon_e \frac{\partial(u_i C_i)}{\partial z} - \varepsilon_e(E + D_m) \frac{\partial^2 C_i}{\partial z^2} = 0 \quad (1)$$

where the first three terms represent accumulation of

solute in the mobile fluid, in the stagnant fluid in the pores and accumulation of the solute adsorbed onto the solid respectively; the fourth term is the result of convective flow and the last term is due to axial dispersion and diffusion.

The pore fluid concentration at the wall, $C_{i,\text{pore}}$, can be related to the fluid concentration outside the pores, C_i , by the mass transfer equation across the surface film (eqn (2)).

$$K_{di}(1 - \varepsilon_e)\varepsilon_p \frac{\partial \bar{C}_{i,\text{pore}}}{\partial t} + \rho_s(1 - \varepsilon_e)(1 - \varepsilon_p) \frac{\partial \bar{q}_i}{\partial t} = k_f a_p [C_i - C_{i,\text{pore}}(R_p)] \quad (2)$$

In this equation k_f is the film mass transfer coefficient in m s^{-1} and a_p is the external surface area per unit particle volume ($\text{m}^2 \text{m}^{-3}$). For spherical particles $a_p = 3/R_p$. The left hand side of eqn (2) describes the accumulation of solute in the particle while the right hand side is the transfer rate across the surface film.

The terms $\bar{C}_{i,\text{pore}}$ and \bar{q}_i are the volume average values inside the porous particles.

$$\bar{C}_{i,\text{pore}} = \frac{3}{R_p^3} \int_0^{R_p} C_{i,\text{pore}} r^2 dr \quad (3)$$

$$\bar{q}_i = \frac{3}{R_p^3} \int_0^{R_p} q_i r^2 dr \quad (4)$$

Equations (1)–(4) must be solved simultaneously with the equilibrium isotherm, initial and boundary conditions. As this set of equations is difficult to solve, it is often assumed to be a lumped parameter expression, thus:

$$\varepsilon_e \frac{\partial C_i}{\partial t} + u_s \frac{\partial C_i}{\partial z} + \rho_p(1 - \varepsilon_e) \frac{\partial \bar{q}}{\partial t} = \varepsilon_e E \frac{\partial^2 C_i}{\partial z^2} \quad (5)$$

$$\rho_p(1 - \varepsilon_e) \frac{\partial \bar{q}}{\partial t} = k_m a_p (C_i - C_i^*) \quad (6)$$

In eqns (5) and (6) the entire particle is treated as having a constant amount of solute adsorbed, \bar{q} , and the stagnant fluid inside the pores is assumed to be in equilibrium with the solid, C_i^* .

The following assumptions have been made in the present work: isothermal operation, constant liquid velocity through the bed, axially dispersed plug flow, negligible accumulation of adsorbate in the pores, solid granules modelled as spheres and linear combination of mass-transfer resistances that leads to:

$$k_m a_p = \frac{1}{\frac{1}{k_f a_p} + \frac{R_p^2}{15\varepsilon_p D_p}} \quad (7)$$

the term $k_m a_p$ being the overall mass transfer coefficient.

With initial conditions:

$$C(z, 0) = C_o$$

$$q(z, 0) = q^*(C_o) \quad (8)$$

and boundary conditions for $t > 0$:

$$\text{at } z = 0, \quad C = C_o$$

$$\text{at } z = L, \quad \partial C / \partial z = 0 \quad (9)$$

3 EXPERIMENTAL

The styrene used in this work was manufactured by Repsol Quimica, SA in Puertollano and Tarragona (Spain). Its main characteristics are detailed in Table 1. The solid sorbent was alumina Compalox AN/V 825, manufactured by Martinswerk. Its main characteristics are also detailed in Table 1.

The operational and constructive data of the industrial columns that operate in Dynasol Elastomeros have been taken as reference to determine the experimental conditions on both a laboratory and a pilot plant scale (Dynasol Elastomeros, private communication). Table 2 shows a summary of the most important constructive and operational data of the adsorption columns at different scales. Two parameters have been considered to be the most relevant in order to analyse the scale-up: superficial velocity of the fluid inside the column and the Reynolds number.^{18,19}

Alumina	Styrene
Commercial name: Compalox ANV-825	Manufacturer: Repsol SA (Spain)
Manufacturer: Martinswerk GmbH	Water content: 100–330 mg kg ⁻¹ ^c
Specific surface: 219.5 ± 5 m ² g ⁻¹ ^a	TBC content: 10 ± 5 mg kg ⁻¹ ^d
d_p distribution: 2.0–5.0 mm ^b	Purity 99.7% minimum ^b
Al ₂ O ₃ 91% minimum ^b	Other impurities: ethyl-benzene (800 mg kg ⁻¹ max), phenyl-acetylene (100 mg kg ⁻¹ max), aldehydes (75 mg kg ⁻¹ max), peroxides (15 mg kg ⁻¹ max), sulfur (30 mg kg ⁻¹ max)

^a Determined by BET specific surface (ASAP 2000 Micromeritics).

^b Data available from supplier documentation.

^c Determined by Karl Fischer coulombimetric titration (DL36 Mettler Toledo).

^d Determined by ASTM D 4590–95^a (UV/VIS Lambda 2 Perkin Elmer).

Table 1. Characteristics of the alumina and styrene used in this work

	Laboratory	Pilot plant	Industrial
Length (m)	0.07 0.14 0.28	0.70	3.66
Inner diameter (m)	3.28×10^{-2}	7.79×10^{-2}	1.20
Section (m ²)	8.45×10^{-4}	4.77×10^{-3}	1.13
Flow (m ³ s ⁻¹)	2.83×10^{-7} 5.50×10^{-7} 1.40×10^{-7}	3.33×10^{-6}	3.33×10^{-4} 5.00×10^{-4} 6.66×10^{-4}
Superficial velocity (m s ⁻¹)	3.35×10^{-4} 6.51×10^{-4} 1.66×10^{-4}	6.99×10^{-4}	2.95×10^{-4} 4.42×10^{-4} 5.89×10^{-4}
Reynolds (10°C)	1.23 2.38 0.608	2.56	1.08 1.62 2.16

Table 2. Constructive and operational data of the adsorption columns

Expt no	Alumina (kg)	Bed length (m)	C_o TBC (mg kg ⁻¹)	F (dm ³ h ⁻¹)	u_s (m s ⁻¹)
1	0.0625	0.070	6.33	1.02	3.35×10^{-4}
2	0.125	0.141	11.66	1.02	3.35×10^{-4}
3	0.250	0.282	11.66	1.02	3.35×10^{-4}
4	0.125	0.141	15.01	1.98	6.51×10^{-4}
5	0.0625	0.070	15.01	1.98	6.51×10^{-4}
6	0.0625	0.070	13.67	0.50	1.66×10^{-4}
7	3.56	0.70	8.50	12.00	6.99×10^{-4}

Table 3. Experimental conditions of the dynamic experiments

Two kinds of experiments were carried out on a laboratory scale:

- (i) *Equilibrium experiments:* A known amount of solid was loaded in a short column and different volumes of liquid circulated through the bed. The initial concentrations of TBC in styrene ranged from 10 mg kg⁻¹ to 20 000 mg kg⁻¹. The solid loading was calculated through a mass balance to the liquid phase after measurement of the initial and final TBC concentrations according to eqn (10).

$$q_i = (C_{o,i}V_o\rho_1 - C_iV\rho_1)/m \quad (10)$$

- (ii) *Dynamic experiments:* Breakthrough curves were obtained through the analysis of the outlet concentration of TBC in styrene with time. Table 3 shows the experimental conditions of the dynamic experiments.

At pilot-plant scale only dynamic experiments were carried out. Operational conditions are also shown in Table 3.

Figure 1 shows the experimental set-up used for the dynamic column experiments carried out in the laboratory. It comprised a jacketed glass column, a peristaltic pump (Gilson Minipuls 3), a cooling system (Polyscience 9510), pressure indicators and two tanks that contained the initial and purified styrene respectively. The equilibrium experiments were carried out in a similar set-up provided also with temperature

control. All the laboratory experiments were carried out under controlled temperature conditions $10(\pm 0.2)^\circ\text{C}$ working with jacketed columns.

In order to carry out experiments at pilot-plant scale a suitable installation was designed and built in the factory of Dynasol Elastomeros.²⁰ Figure 2 shows a flow diagram of the pilot plant set-up. It consisted of a tank of 0.2 m³ capacity that included a level control that permitted filling from a main container of styrene as soon as its level decreased. The fluid was pumped by a metering pump (Bran & Luebbe, E-P31) provided with a frequency variator (Novat Series D) and a

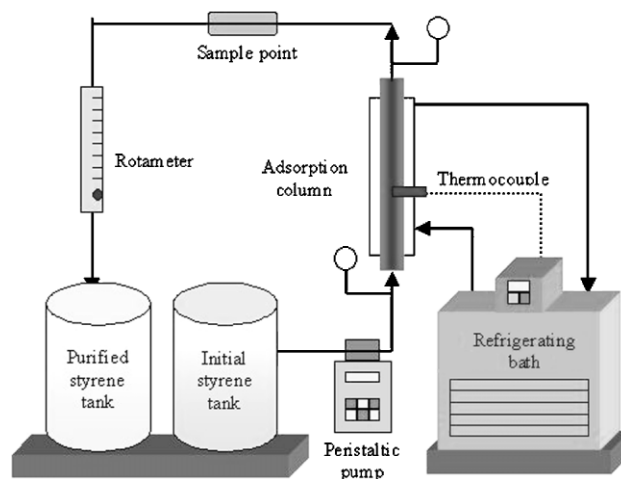


Figure 1. Experimental set-up used in the laboratory dynamic experiments.

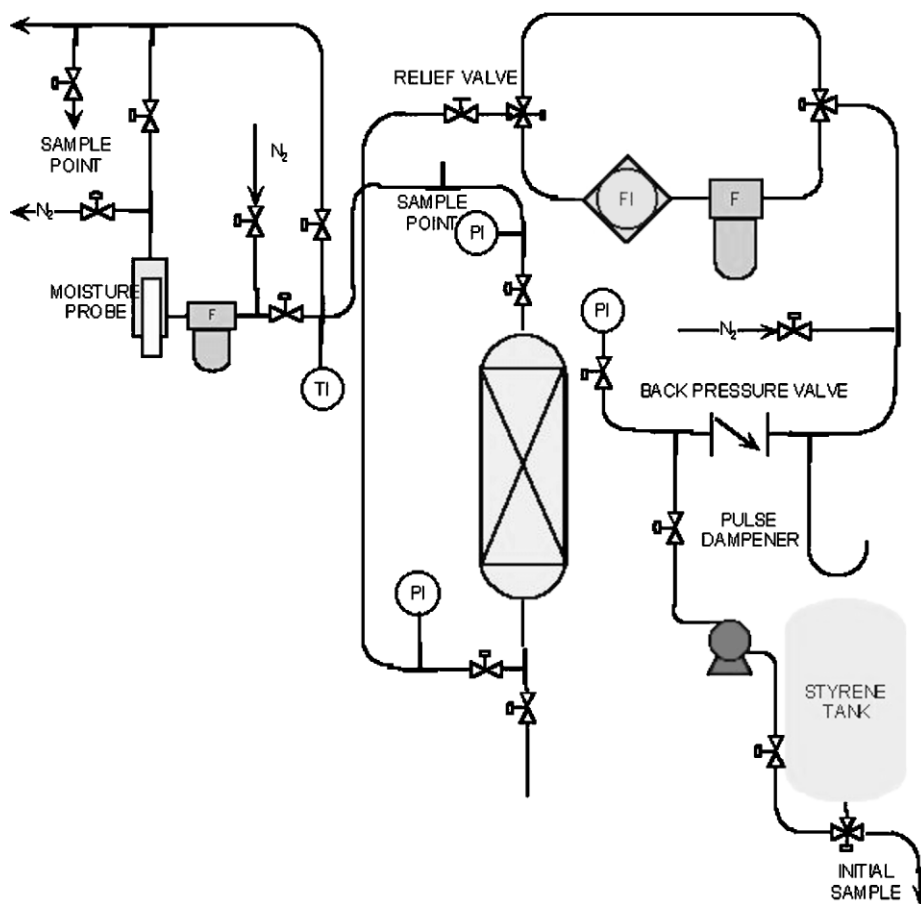


Figure 2. Experimental set-up used in the adsorption pilot plant.

hydropneumatic pulse dampener (Olaer) to eliminate pulsation in the pumped fluid. The system incorporated a basket filter (Bopp & Reuther, DN10 PN40) placed before the flow meter (Bopp & Reuther, OI03Ag41/A4, DN6). The fixed bed column was made of steel; its length was 0.70m and its inner diameter was 7.79×10^{-2} m. To register the temperature evolution a thermocouple type K (Cole Palmer) and a register (Testo, 922) were installed. In the pilot plant set-up it was not possible to control the temperature of the column and therefore experiments were performed at ambient temperature. The pilot plant was also provided with a line of dry cyclohexane and nitrogen that allowed all the equipment to be kept clean in order to avoid styrene polymerisation.

The analysis of the concentration of TBC in styrene was carried out following the ASTM standard D 4590-95^a ‘Standard Test Method for Colorimetric Determination of *p-tert*-Butylcatechol in Styrene Monomer or AMS (α -Methylstyrene) by Spectrophotometry’, with a spectrophotometer (Perkin Elmer, Lambda 2). Absorbance measurements data in the range of work varied between 0.000 and 0.075 absorbance.

4 RESULTS AND DISCUSSION

4.1 Laboratory-scale studies

Experimental equilibrium data for the adsorption of

TBC from styrene onto alumina in the wide range of concentration and working at a temperature of 10 °C are shown in Fig 3. They were fitted by the Sips equation (Langmuir–Freundlich),^{10,21} eqn (11).

$$q = \frac{1.73 \times 10^{-3} C^{0.50}}{1 + 8.36 \times 10^{-3} C^{0.50}} \quad (11)$$

where q is kg TBC kg⁻¹ alumina and C is mg TBC kg⁻¹ styrene.

The value of the weighted standard deviation (sd)

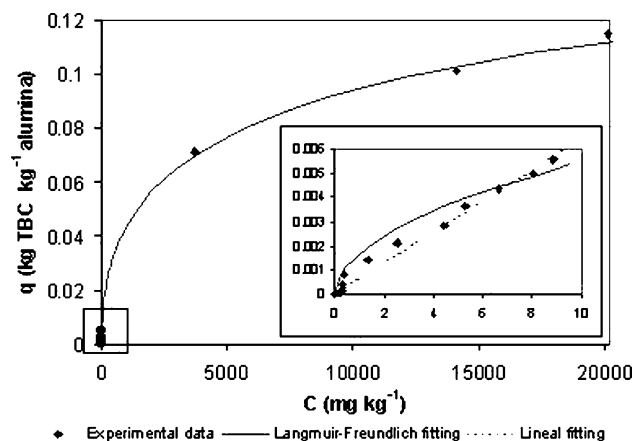


Figure 3. Adsorption isotherm at 10 °C.

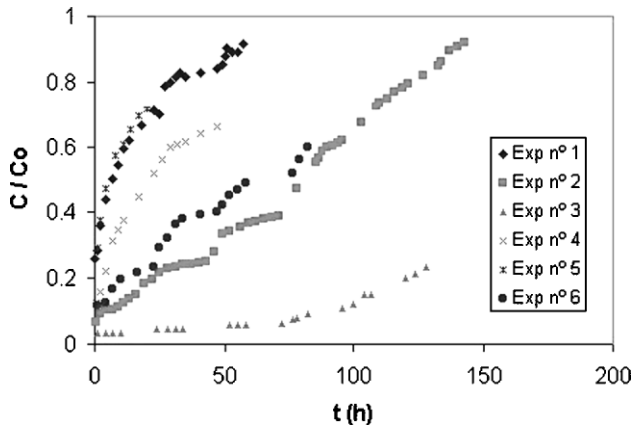


Figure 4. Breakthrough curves for TBC adsorption onto alumina obtained from laboratory experiments.

defined according to eqn (12) was 3.38%.

$$sd = \sqrt{\frac{\sum (C_{exp} - C_{sim})^2}{n - 1}} \quad (12)$$

Considering that the usual range of concentration of TBC in styrene is less than 15 mg kg^{-1} , Fig 3 shows the fitting of eqn (11) to experimental data in the range of 0 mg TBC kg^{-1} styrene to $10 \text{ mg TBC kg}^{-1}$ styrene, obtaining a value of the weighted standard deviation, with the data in the latter range, of 8.46%. However, to facilitate numerical resolution of model equations, eqns (1)–(9), the linear regression of experimental data was tried in the lower range of TBC concentration. Equation (13) correlated satisfactorily equilibrium data at 10°C with a value of the sd of 4.92%, Fig 3.

$$q = 6.42 \times 10^{-4} C \quad (13)$$

The linear form is often approximated at very low concentrations such as those used in this work.^{21–23} Linear isotherms have been used in the adsorption of water from styrene²⁴ and water from benzene for concentrations lower than 0.3 kg m^{-3} ²⁵ and in the

adsorption of several organic compounds such as 1-methylnaphthalene or *p*-xylene from benzene onto alumina.¹⁴

Basically, the linearity shows that the number of sites for adsorption remains constant; ie as more solute is adsorbed more sites must be created. Such a situation could arise when the solute has a higher attraction for the substrate molecules than the solvent itself has. This behaviour has been found to occur in several types of systems such as in the adsorption of aromatic solutes on hydrophobic polymers; benzene in *n*-heptane as solute adsorbed on dry wool fibre or certain amino acids in water on silica dust.²⁶

After the analysis of the adsorption equilibrium, dynamic experiments were carried out in order to obtain breakthrough curves by measuring the solute concentration in the outlet stream. Also, these curves will be used to determine the total amount of TBC adsorbed onto the solid. Finally, breakthrough data will be useful to determine the mass transport parameters of the model proposed to describe the adsorption process.

Figure 4 shows the experimental breakthrough curves obtained in the laboratory set-up. Experimental data did not reach saturation of the column because this would require lengthy experimental work and a large amount of styrene. Experiment 2 was carried out close to solid saturation. The value of TBC adsorbed onto the alumina was $0.006 \text{ kg TBC kg}^{-1}$ alumina, a value that was very close to the adsorption capacity calculated from the experimental isotherm.

4.2 Model parameters

The external porosity of the bed, ϵ_e , has been determined experimentally by direct measurement, obtaining a value of 0.256. The particle density value, ρ_p , has been taken from literature from data of several aluminas with similar values of specific surface.^{10,13}

The parameters related to mass transfer in the previously described model, the way they have been obtained and their values are shown in Table 4. The

Table 4. Parameters associated with the mathematical model of the adsorption of TBC onto alumina

Parameter	Reference	Value
Molecular diffusivity, D_m	Wilke-Chang (1965)	$1.02 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$
	$D_{AB} = \frac{7.4 \times 10^{-8} (\psi_B M_B)^{1/2} T}{\mu_{AB} V_{bA}^{0.6}}$	
Axial dispersion coefficient, E	Levenspiel (1999) ³⁰	$F=0.50 \text{ l h}^{-1} \quad 3.40 \times 10^{-6} \text{ m}^2 \text{ s}^{-1}$ $F=1.02 \text{ l h}^{-1} \quad 6.87 \times 10^{-6} \text{ m}^2 \text{ s}^{-1}$ $F=1.98 \text{ l h}^{-1} \quad 1.33 \times 10^{-5} \text{ m}^2 \text{ s}^{-1}$
Mass transfer coefficient, k_m	$k_m a_p = \frac{1}{\frac{1}{k_f a_p} + \frac{R_p^2}{15 \epsilon_p D_p}}$	$F=0.50 \text{ l h}^{-1} \quad 6.78 \times 10^{-3} \text{ s}^{-1}$ $F=1.02 \text{ l h}^{-1} \quad 7.37 \times 10^{-3} \text{ s}^{-1}$ $F=1.98 \text{ l h}^{-1} \quad 7.88 \times 10^{-3} \text{ s}^{-1}$
Film diffusion coefficient, k_f	Wilson–Geankoplis (1966) ³¹	$F=0.50 \text{ l h}^{-1} \quad 1.03 \times 10^{-5} \text{ m s}^{-1}$ $F=1.02 \text{ l h}^{-1} \quad 1.30 \times 10^{-5} \text{ m s}^{-1}$ $F=1.98 \text{ l h}^{-1} \quad 1.62 \times 10^{-5} \text{ m s}^{-1}$
	$Sh = (1.09/\epsilon_e) Re^{1/3} Sc^{1/3}$	
Diffusivity in pores, D_p	Estimated from the experimental breakthrough curves	$3.96 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$

means of obtaining the value of the pore diffusivity, D_p , will be explained in detail in the following paragraphs.

This system of coupled partial differential equations plus the adsorption isotherm and the accompanying initial and boundary conditions have been solved using gPROMS software (general PROcess Modelling System, version 1.6B) developed by Process Systems Enterprise Ltd. The part of this software called gEST allows the estimation of the values of the model parameters. So, the equations of the model and the breakthrough curves have been introduced in this software, and after integration, the value of the parameter D_p that led to the minimum weighted standard deviation between experimental and predicted data was selected. Figure 5 illustrates this procedure.

The best fitting has been obtained for a value of D_p of $3.96 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$ with an sd of 5.81%.

Literature references that report the value of this parameter for similar systems are very scarce although some values have been found which are close to $10^{-9} \text{ m}^2 \text{ s}^{-1}$. Joshi and Fair,²⁷ working with toluene drying on alumina, concluded that around 70% of the global resistance to mass transfer was in the pores and reported a value for D_p of $8.00 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$. For the adsorption of water from styrene onto alumina a value of $6.10 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$ was found.²⁴ Similar conclusions have been obtained by other authors.¹¹ In the adsorption of organic compounds a value of $2.5 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$ has been found for the adsorption of phenol onto activated carbon²⁸ or values between 1.47 and $1.68 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$ for the adsorption of xylenes onto zeolites.²⁹ The most relevant study found in the literature deals with the adsorption of naphthalene, coronene, octa-ethylporphyrin and tetra-phenylporphyrin from cyclohexane onto alumina where values of D_p of $4.3 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$ have been reported for a certain type of alumina.¹⁷

Figures 6 and 7 show some of the experimental and

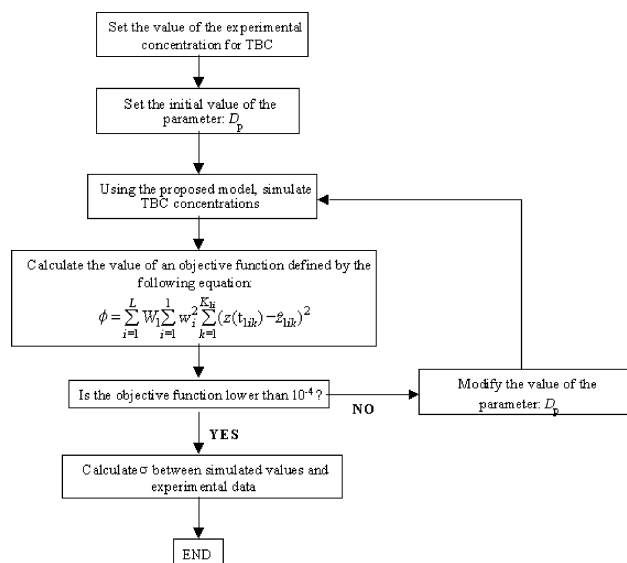


Figure 5. Flowchart of the parameters' estimation procedure.

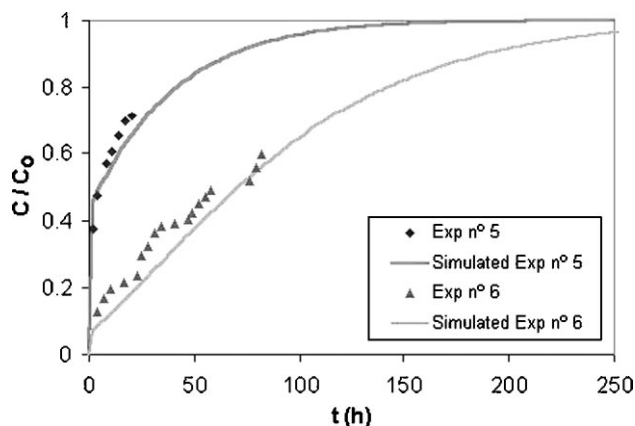


Figure 6. Experimental and predicted breakthrough curves (bed length=0.070m).

predicted breakthrough curves for different bed lengths and flow rates. It is observed that the predicted breakthrough curves agree satisfactorily with the experimental data.

4.3 Pilot-plant studies

Once the mathematical model and characteristic parameters had been obtained from laboratory studies they were used to simulate the behaviour of the adsorption of TBC in styrene onto alumina in a different scale. A pilot plant was built which operated with the same flow regime as in the experiments carried out at laboratory-scale.²⁰ With the proposed model and the corresponding parameters a simulation of a breakthrough curve for the pilot plant conditions was made and it was compared with experimental data, as shown in Fig 8. From this figure it can be deduced that the experimental data are well described by the predicted breakthrough curve; therefore the validity of the presented model and the parameters obtained to describe the process on a larger scale has been confirmed.

The final step in this study has been the description of the industrial process using the model and par-

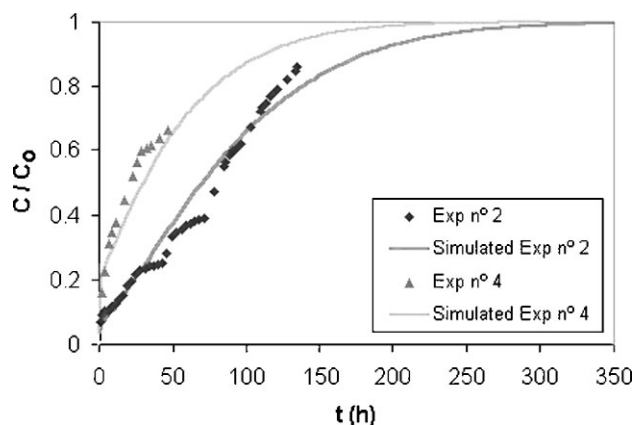


Figure 7. Experimental and predicted breakthrough curves (bed length=0.141m).

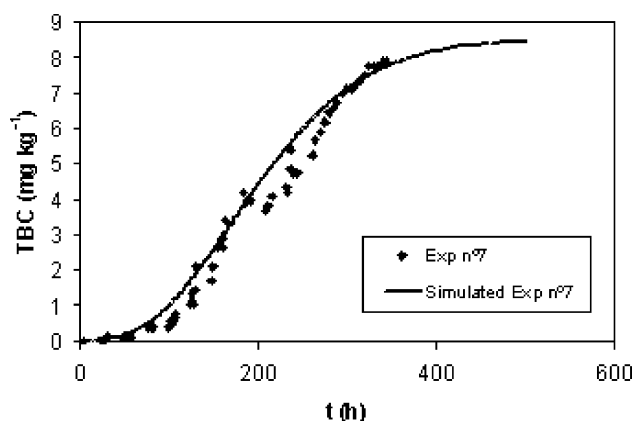


Figure 8. Experimental and predicted breakthrough curves for pilot-plant scale.

ameters previously obtained. Its constructive and operational data, shown in Table 2, as well as the corresponding parameters, have been introduced in the mathematical model and the simulated breakthrough curves corresponding to different operation flow rates are shown in Fig 9.

For the industrial production of synthetic rubber the amount of TBC in the styrene entering the polymerisation reactor must be less than 1 mg kg^{-1} . According to the simulated breakthrough curves shown in Fig 9 the maximum time a fixed bed can be working for the purification of styrene is in the range of 850 h to 1700 h for fluids flow rates of $20 \text{ dm}^3 \text{ min}^{-1}$ to $40 \text{ dm}^3 \text{ min}^{-1}$. These data are very useful for optimising the behaviour of alumina beds and the model can be applied to predict the breakthrough time to changes in flow rate or the initial concentration of TBC while keeping the same flow regime and range of concentrations.

5 CONCLUSIONS

In this work the model and parameters of the adsorption process of 4-*tert*-butylcatechol (TBC) in styrene onto alumina have been obtained.

This purification process is very important in the

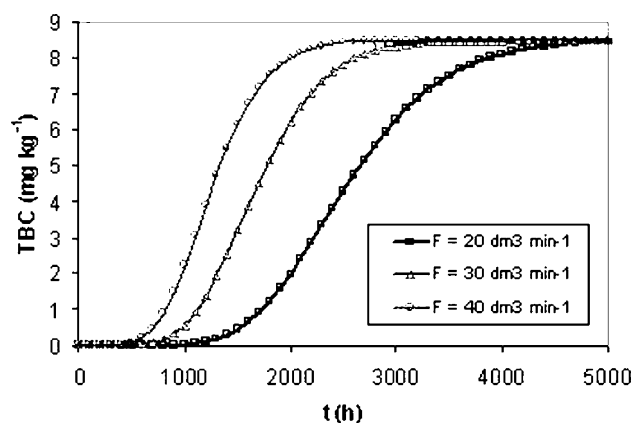


Figure 9. Simulations of the industrial process for several flow rates.

manufacture of synthetic rubber and several plastic materials where high volumes of styrene are employed.

First, the study of the adsorption equilibrium in the range of concentrations of TBC between 0 and $20\,000 \text{ mg kg}^{-1}$ onto alumina at 10°C has been carried out. Experimental data fit the equation:

$$q = \frac{1.73 \times 10^{-3} C^{0.50}}{1 + 8.36 \times 10^{-3} C^{0.50}}$$

where q is kg TBC kg^{-1} alumina and C is mg TBC kg^{-1} styrene with an sd value of 3.38%. For initial concentrations lower than 15 mg kg^{-1} in styrene, which represent usual conditions in the industrial process, the equilibrium was approximated to the linear equation $q = 6.42 \times 10^{-4} C$ with an sd value of 4.92%.

Breakthrough curves have been obtained from dynamic experiments carried out in a laboratory set-up and have been used to estimate the pore diffusivity parameter of the mathematical model, finding a value of $D_p = 3.96 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$ that is in the range of the values reported in the literature for several systems.

A pilot plant has been designed and built to carry out experiments on a larger scale in order to verify the validity of the mathematical model and parameters that have been obtained previously. Experimental data are well described by the predictions made with the mathematical model. This enables the industrial process to be simulated, a procedure which is already in operation and which can be a useful tool in process control and optimisation.

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